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Quantum magnetism : novel materials and phenomena

Indrani Bose
Department of Physics, Bose Institute, 93/1, A. P C Road,
Calcutta-700 009, India

Abstract : The subject of quantum magnetism has witnessed a tremendous surge in research activity in the last decade Several new materials and phenomena have been discovered which have made significant additions to our knowledge about magnetic systems In this review, some of the important developments will be discussed with appropriate examples

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1. Introduction

In the last ten years or so, there has been unprecedented research activity in the area of magnetism. Many new materials exhibiting novel phenomena have been discovered. In this review, we will discuss some of these exciting developments. The discovery of high-temperature superconductors in 1986 has given a tremendous boost to research on quantum antiferromagnets (AFMs) [1]. The high-T_c materials are cuprate systems with a layered structure. The common structural ingredient is the copper-oxide plane. All the dominant electronic and magnetic properties are associated with the plane The plane looks like a square lattice. The copper ions carrying spin-1/2 sit at the lattice sites and the oxygen ions are on the bonds in between The copper ions interact through AFM superexchange interaction mediated *via* oxygen ions. The interaction Hamiltonian is the well-known Heisenberg Hamiltonian given by

$$H = \sum J_{ij} S_i . S_j$$

S_i, S_j are the spins located at the sites i and j, J_{ij} denotes the strength of the exchange interaction. Usually, i, j are nearest-neighbours (NNs) but further-neighbour interactions are also important for many real systems. In most materials J_{ij}'s are assumed to be equal to the value J. The magnitude of spins may be 1/2, 1, 3/2, 2, ... *etc*. For positive J, NN spins favour antiparallel orientation to achieve the lowest energy state, this is the case of antiferromagnetism. For ferromagnetism, J is −ve and the NN spins favour parallel orientation. For the cuprate systems, J is +ve and $S = 1/2$.

Consider the cuprate system La_2CuO_4 This system is an AFM and an insulator. Replacement of La ions by Sr or Ba ions is called doping and x in $La_{2-x}Sr_xCuO_4$ is called the dopant concentration. The effect of doping is to replace some of the Cu spins in the CuO_2 planes by positively charged holes. On doping with a few percent of holes, the long range AFM order is rapidly destroyed leaving behind a spin-disordered state This has motivated a large number of studies of quantum AFMs with spin-disordered states as ground states. Some of these AFMs constitute a class known as spin-gap (SG) systems. In Section 2, the SG systems will be introduced In Section 3, doped SG antiferromagnets will be discussed. The doped cuprate systems exist in insulating, metallic and superconducting phases depending on the temperature and dopant concentration The doped systems exhibit strange properties which cannot be explained by conventional theories. This has motivated the study of other doped quantum AFMs to gain a proper understanding. Section 4 contains some more examples of recent developments in the area of magnetism.

2. Spin-gap antiferromagnets

Recently, several new AFM compounds have been discovered which exhibit the phenomenon of SG. Excitations in a magnetic system are created by deviating spins from their ground state arrangement The energy E of the excitation is a function of the momentum wave vector k The excitation spectrum is said to be gapless if there is at least one momentum wave vector at which the excitation energy becomes zero. The excitation spectrum has a SG if the lowest excitation is separated by an energy gap from the ground state. The SG occurs naturally in systems with anisotropies of various types The SG in the new AFM systems, however, has a purely quantum origin and cannot be ascribed to any anisotropy effect SG implies the absence of low-energy spin excitations This is reminiscent of the energy gap in the electronic excitation spectrum of a superconductor (SC) The gap opens up due to the formation of bound Cooper pairs of electrons in the SC state For temperature $T > T_c$, the SC gap disappears and the system becomes a normal metal. In most of the SG systems, the ground state consists of singlets $\left(\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow\right)$ of spins which are spin pairs, the analogues of Cooper pairs. In the SC ground state, long range phase coherence is established, all the Cooper pair wave functions have the same phase The singlet ground state of the SG systems also have long range coherence characterised by novel order parameters [2]. The ordering is lost above a temperature T_c. Recently experiments on the cuprate systems show the evidence of partial spin and charge gaps opening up for $T > T_c$ [3]. The gap has been designated as the pseudogap and may indicate some kind of pairing without phase coherence above T_c. In a conventional SC, pair formation and opening up of the energy gap occur simultaneously at T_c. The effect of doping on the magnitude of the pseudogap and its evolution to the SC energy gap below T_c are some of the issues that are yet to be settled. Study of doped SG AFMS may lead to knowledge about the various possibilities.

We will now discuss some AFM spin-gap systems which have been discovered in the last five years. The most well-known example of a SG system is a Haldane-gap AFM. These systems are linear chain systems with integer spins. Half-odd integer spin chains, on the other hand, have a gapless excitation spectrum. The compound Y_2BaNiO_5 is an example of a $S = 1$ linear chain AFM that can be doped with holes [4]. The ground state is spin-disordered and can be characterised as a quantum spin liquid (QSL). The system offers the first example of a doped QSL in 1 d. The doped and spin-disordered CuO_2 plane of the cuprate systems is an example of a QSL in $d = 2$ The holes are introduced by replacing yttrium with calcium. Experimentally, there is a large reduction in the DC resistivity as the dopant concentration increases from zero. At the same time, new states appear within the spin-gap. As in the case of the CuO_2 plane, the holes move in a background of antiferromagnetically interacting spins

The linear chain $S = 1/2$ AFM compound $CuGeO_3$ is the first example of an inorganic compound showing the spin-Peierls (SP) transition [5] This transition is caused by the coupling of spins to the phonons, the quanta of lattice vibrations, in the system. Below T_{SP}, the SP transition temperature, the 1 d lattice distorts bringing successive pairs of spins closer. As a result, a gap opens up in the excitation spectrum below T_{SP}. Next, we turn to the discussion of spin ladders [6]. The spins have magnitude 1/2. The simplest spin-ladder consists of two chains coupled by rungs and interpolates between 1 d and 2 d AFMs. The Hamiltonian is given by

$$H_L = J_\perp \sum_{\text{rungs}} S_i . S_j + J_\parallel \sum_{\text{chains}} S_i . S_j \tag{2}$$

where $J_\parallel$ and $J_\perp$ are the exchange interactions along the chains and rungs respectively. The ladder has a gap in the excitation spectrum even in the isotropic coupling limit $J_\parallel = J_\perp$. The ground state consists of singlets along the rungs. An excitation is created by replacing one of the singlets by a triplet and then letting it propagate. The triplet excitation spectrum exhibits a gap. A general spin-ladder consists of n chains. One example of such a system is $Sr_{n-1}Cu_{n+1}O_{2n}$ (n = 3, 5, 7, ...) which consists of ladders of $(n+1)/2$ chains with frustrated "trellis" coupling between the ladders [7]. A ladder with an odd number of chains has properties similar to that of a single chain, namely, gapless excitation spectrum and a power-law decay of the spin-spin correlation function. A ladder with an even number of chains has a spin-gap and an exponential decay of the spin-spin correlation function. The significant difference between the properties of odd and even chain ladders has been verified in a number of experiments [6]. The system $La_{4+4n}Cu_{8+2n}O_{14+8n}$ also has a ladder-like structure. Another compound of interest is $LaCuO_{2.5}$ [8]. Initial susceptibility experiments were interpreted as showing a gap in the excitation spectrum but subsequent μ sr and NMR experiments indicate an AFM transition below $T_N \sim 110$ K. The compound $Cu_2(C_5H_{12}N_2)_2Cl_4$ is also an example of a two-chain ladder compound [9]. Magnetic susceptibility results indicate the presence of weak FM diagonal interactions in the ladder. The compound $A_{14}Cu_{24}O_{41}$ (A = Ca, Sr, Ba, La, Y) is composed of layers containing two-chain ladders alternating with layers of CuO_2 chains [10]. Spin-gaps have been seen in the excitation spectra of both the chains and the ladders. A recent addition to the list of AFM systems exhibiting SG is the compound CaV_4O_9 [11]. The lattice structure of this compound corresponds to the 1/5-depleted square lattice. In this lattice, 1/5 of the original lattice sites of the square lattice are missing. The lattice consists of four-spin plaquettes connected by bonds. Susceptibility, NMR spin-lattice relaxation rates and neutron scattering measurements show the existence of a SG in the excitation spectrum. The spin model on the CaV_4O_9 lattice has been suggested to be in the Plaquette Resonating Valence Bond (PRVB) phase and includes both NN as well as further-neighbour interactions [12]. In the PRVB phase, the four spins in each plaquette is in a RVB spin configuration. The PRVB state is a linear superposition of two singlet states. In one state, spin singlets form along the two horizontal bonds and in the other state, the singlets are along the two vertical bonds. The spin-disordered state of the doped CuO_2 plane in the high-T_c cuprate systems has earlier been conjectured to be in a RVB state. CaV_4O_9 provides the first example of a 2*d* AFM system in which the possibility of the RVB state is supported by experimental evidence. CaV_4O_9 is the member of a class of compounds, CaV_nO_{2n+1} ($n = 2 - 4$) which are defined on a $1/(n+1)$-depleted square lattice [13]. The excitation spectrum is gapless (with gap) when n is odd (even) This behaviour is similar to that found in spin-ladders and half-odd integer and integer spin chains.

3. Doped spin-gap antiferromagnets

The high-T_c cuprate systems have a rich phase diagram as a function of temperature and dopant concentration [1]. In the undoped state, the cuprate system is an AFM as well as an insulator where the insulating property is brought about by strong Coulomb correlation. On the introduction of a few percent of holes, there is an insulator-to-metal (MI) transition. The underdoped metallic state is characterised by unconventional transport and thermodynamic properties which cannot be explained by the Fermi liquid theory of conventional metals. There is a conjecture that AFM spin fluctuations may be responsible for the unusual properties. There is experimental evidence that short-range AFM correlations persist in the metallic as well as SC phases. In the SC state of the cuprates, the holes bind in pairs. In a conventional SC, the bound pairs, the so-called Cooper pairs, consist of electrons rather than holes. The binding mechanism of the holes in the cuprates is not as yet well-understood. A class of theories suggest that exchange of AFM spin fluctuations may cause the binding of holes [14]. This is in contrast to the fact that in conventional SCs electrons bind on exchange of phonons. There has been a large number of studies on quantum AFMs doped with holes in order to explore various possibilities. Even at the level of a single hole, one encounters a non-trivial many-body problem, one hole in a background of a large number of antiferromagnetically interacting spins [15]. Strong correlation demands that no site is doubly occupied by electrons to minimize the Coulomb repulsion energy. A hole as soon as it moves, leaves behind its wake a string of wrongly oriented (parallel) spin pairs, thus raising the energy associated with the AFM exchange interaction. Antiferromagnetism favours antiparallel spin pairs. Thus there is a competition between kinetic energy lowering due to hole delocalization and exchange energy minimization. This competition can give rise to novel types of ordering in the ground state. For example, combined ordering of charge and spin can occur. This is seen in the hole doped AFM compound La_2NiO_4 which is not a SC. The ordering consists of domains of antiferromagnetically ordered spins separated by periodically spaced domain walls to which the holes segregate [16].

The problem of doped spin ladders has been addressed in a large number of theoretical studies. Dagotto *et al* [1,6,17] first suggested the possibility of SC in a two-chain ladder system. Two holes are predominantly on the same rung to minimise the loss in exchange interaction energy. This gives rise to an effective binding of holes. Bose and Gayen have constructed a spin-ladder model which includes diagonal hopping and exchange interaction terms alongwith the corresponding intra-chain and inter-chain terms. The Hamiltonian describing the system is the well-known t-J Hamiltonian. The kinetic energy term describes the hopping of holes to sites separated by NN and diagonal distances. The holes move by displacing spins. The spins interact *via* Heisenberg AFM exchange interaction. Bose and Gayen [18–21] have derived a number of exact results (ground state and excited states) for the cases of zero hole, one hole, two holes as well as more than two holes. The most important result is that of the binding of a pair of holes [20]. The effects of both strong correlation and quantum fluctuations have been exactly taken into account to derive the results. Hiroi and Takano succeeded in doping a spin-ladder compound $La_{1-x}Sr_xCuO_{2.5}$ [22]. The compound showed a MI transition as x was changed but unfortunately no SC was observed. Considerable excitement was created when hole SC was found in the spin-ladder compound $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$ under a pressure of 3 to 4.5 GPa [23]. T_c is not high and is of the order of 9 K and 12 K respectively. There is some experimental evidence to suggest that the spin-gap collapses when SC is stabilised under 29 kbar pressure [24]. Studies on this system and its variants are still at an early stage. Doping of the ladder systems leads to novel phenomena and poses a number of challenging problems.

Other examples

The present review has been mainly devoted to the description of SG AFMs and their connections with high-T_c cuprate systems. A brief discussion of the latter has been included to explain the current research interest in quantum AFMs. Much of the knowledge and insight that have been gained so far have expanded the scope and content of the subject of magnetism. The new magnetic materials that have been discovered are interesting in their own right apart from their possible relevance in the context of cuprate systems. Besides SG AFMs, a number of recent discoveries have opened up new areas of research in magnetism. In the following, we describe some of these discoveries briefly.

Random $S = 1/2$ chains are the latest class of novel $1d$ compounds to be discovered. The compound $Sr_3CaPt_{0.5}Ir_{0.5}O_6$ can be described as a $S = 1/2$ Heisenberg chain with randomly distributed ferromagnetic (FM) and AFM exchange interaction bonds [25]. The random spin chain is a quantum mechanical system with disorder. The surprising experimental result is that at low temperatures, when quantum effects are supposed to be dominant, the susceptibility behaviour is that of a spin system consisting of classical free spins. The experimental observation has motivated further studies on random spin systems. The second example is that of quantum hysteresis in molecular magnets [26]. Magnetic materials are characterised by hysteresis. Their response to an increasing magnetic field is not the same as that in a decreasing field. The hysteresis loop obtained as a smooth shape. Recently, material scientists have fabricated a crystalline organic compound Mn_{12}-acetate consisting of weakly interacting molecules of giant spin 10. Magnetization measurements made at a temperature below a few degrees kelvin show a hysteresis loop containing steps. The phenomenon is believed to be caused by macroscopic quantum tunneling of the magnetic moment associated with the giant spin. The next example is that of light-induced magnetization in a cobalt-iron cyanide complex. The system orders magnetically below a critical temperature of 16 K. Sato *et al* found an increase in the critical temperature from 16 K to 19 K by shining red light on the system [27]. On shining with blue light, the enhancement of the magnetization can be partly removed. Such control over magnetic properties by optical signals may be of significance in the design of magneto-optical devices. The last example is that of colossal magnetoresistance (CMR) [28]. Magnetoresistance is the relative change in the electrical resistance of a material on the application of a magnetic field. All metals show MR but only a few percent. The phenomenon offers prospects for applications such as reading heads in hard disk drives and digital videotape recorders. A device whose conductivity is sensitive to magnetic changes would be ideal for quick conversion of magnetically stored information into electrical signals. Some years back, a 220% resistance change was achieved at T = 1.5 K in a multilayer of 50 alternating films of iron and chromium. An even more dramatic effect that has been observed recently is that of CMR. This has been seen in perovskite magnates of the type $La_{1-x}A_xMnO_3$ where A is a divalent cation such as an alkaline earth (Sr^{2+}, Ca^{2+}, Ba^{2+} *etc.*) or Pb. CMR involves resistivity changes as large as several thousand percent. The effect can only be seen at low T and high magnetic fields. Research on the CMR materials has benefitted from the study of high-T_c cuprate systems. The CMR materials also have a rich phase diagram which has motivated a large number of studies, both theoretical and experimental, to understand the origin of the various phases. To summarise, we have discussed in this review various new magnetic phenomena and materials which have led to unprecedented research activity in the area of magnetism. Many problems still remain to be solved which imply continuing research activity in the coming years.

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